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(54) **Cement composition**

(57) A method and cement composition is provided for sealing a subterranean zone penetrated by a well bore, wherein the cement composition comprises zeolite, cementitious material, and water sufficient to form a slurry.

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Description

[0001] The present invention relates generally to a cement composition for sealing a subterranean zone penetrated by a well bore.

[0002] In the drilling and completion of an oil or gas well, a cement composition is often introduced in the well bore for cementing pipe string or casing. In this process, known as "primary cementing," the cement composition is pumped into the annular space between the walls of the well bore and the casing. The cement composition sets in the annular space, supporting and positioning the casing, and forming a substantially impermeable barrier, or cement sheath, which isolates the well bore from subterranean zones.

[0003] Changes in pressure or temperature in the well bore over the life of the well can produce stress on the cement composition. Also, activities undertaken in the well bore, such as pressure testing, well completion operations, hydraulic fracturing, and hydrocarbon production can impose stress. When the imposed stresses exceed the stress at which the cement fails, the cement sheath can no longer provide the above-described zonal isolation. Compromised zonal isolation is undesirable, and necessitates remedial operations to be undertaken.

[0004] Due to its incompressible nature, neat cement is undesirable for use where there is a chance of expansion or contraction in the well bore. In the past, components such as fumed silica have been added to lower the Young's modulus of cement compositions. However, fumed silica is often subject to shortages, and hence to undesirable variations in costs.

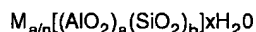
[0005] We have now devised a cement composition that can provide elasticity and compressibility, while retaining high compressive and tensile strengths.

[0006] In one aspect, the present invention provides a cement composition for sealing a subterranean zone penetrated by a well bore, which composition comprises zeolite, cementitious material, and water sufficient to form a slurry.

[0007] In another aspect, the invention provides a method of sealing a subterranean zone penetrated by a well bore, which method comprises cementing the zone with a cement composition of the invention.

[0008] A variety of cements can be used in the present invention, including cements comprised of calcium, aluminum, silicon, oxygen, and/or sulfur which set and harden by reaction with water. Such hydraulic cements include Portland cements, pozzolan cements, gypsum cements, aluminous cements, silica cements, and alkaline cements. Portland cements of the type defined and described in API Specification 10, 5th Edition, July 1, 1990, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety) are preferred. API Portland cements include Classes A, B, C, G, and H, of which API Classes A and C are particularly preferred for the present embodiment. The desired amount of cement is understandably dependent on the cementing operation.

[0009] Zeolite is a porous aluminosilicate mineral that may be either a natural or manmade material. It is understood that for the purpose of this patent application, the term "zeolite" refers to and encompasses all natural or manmade forms. All zeolites are composed of a three-dimensional framework of SiO_4 and AlO_4 in a tetrahedron, which creates a very high surface area. Cations and water molecules are entrained into the framework. Thus, all zeolites may be represented by the formula:



where M is a cation such as Na, K, Mg, Ca, or Fe; and the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5. Some common examples of zeolites include analcime (hydrated sodium aluminum silicate); chabazite (hydrated calcium aluminum silicate); harmotome (hydrated barium potassium aluminum silicate); heulandite (hydrated sodium calcium aluminum silicate); laumontite (hydrated calcium aluminum silicate); mesolite (hydrated sodium calcium aluminum silicate); natrolite (hydrated sodium aluminum silicate); phillipsite (hydrated potassium sodium calcium aluminum silicate); scolecite (hydrated calcium aluminum silicate); stellerite (hydrated calcium aluminum silicate); stilbite (hydrated sodium calcium aluminum silicate); and thomsonite (hydrated sodium calcium aluminum silicate).

[0010] Zeolites are widely used as cation exchangers, desiccants, solid acid catalysts, and absorbents. We believe that in cement compositions, zeolites enhance the compressive strength and decrease porosity as a result of pozzolanic reaction, similar to that of conventional pozzolans such as fly ash, fumed silica, slag, and diatomaceous earth. As shown in the following examples, zeolites provide enhanced properties in a number of oil well cementing applications, creating lightweight slurries. For example, at low temperatures, the pozzolanic reaction produces increased early compressive strength development. Furthermore, the zeolite cement slurries of the present embodiments exhibit thixotropic properties which can be of benefit in such applications as gas migration control, lost circulation and squeeze cementing. Moreover, the zeolite cement slurries of the present embodiments impart fluid loss control qualities, thereby maintaining a consistent fluid volume within a cement slurry, preventing formation fracture (lost circulation) or flash set (dehydration).

[0011] In one composition of the invention, zeolite is present in an amount of about 1% to about 95% by weight of

the cement, and more preferably in an amount of about 5% to about 75% by weight of the cement. In another composition, zeolite may be used as an extender for lightweight slurries. In this use, the zeolite is present in an amount of about 30% to about 90% by weight of the cement, and more preferably in an amount of about 50% to about 75% by weight of the cement. It is to be understood that the above-described zeolite cement mixtures can be used as lightweight cements, normal weight cements, densified cements, and squeeze cements. Moreover, zeolite may be used as a suspending aid, thixotropic agent, particle packing agent, strength retrogression prevention agent, strength enhancer, foamed cement-stability agent, and a low temperature accelerator.

[0012] Water in the cement composition is present in an amount sufficient to make a slurry which is pumpable for introduction down hole. The water used to form a slurry in the present embodiment can be fresh water, unsaturated salt solution, including brines and seawater, and saturated salt solution. Generally, any type of water can be used, provided that it does not contain an excess of compounds, well known to those skilled in the art, that adversely affect properties of the cement composition. The water is present in an amount of about 22% to about 200% by weight of the cement, and more preferably in an amount of about 40% to about 100% by weight of the cement.

[0013] In an alternative, conventional accelerating additives such as sodium chloride, sodium sulfate, sodium aluminate, sodium carbonate, calcium sulfate, aluminum sulfate, potassium sulfate, and alums can be added to further increase early compressive strength development of the cement composition. The accelerating additives are present in an amount of about 0.5% to about 10% by weight of the cement, and more preferably in an amount of about 3% to about 7% by weight of the cement.

[0014] Conventional dispersants may be added to control fluid loss, such as a sulfonated acetone formaldehyde condensate available from SKW Polymers GmbH, Trostberg, Germany. The dispersant is preferably present in a range from about 0.01 % to about 2%.

[0015] A variety of additives may be added to the cement composition to alter its physical properties. Such additives may include slurry density modifying materials (e.g., silica flour, sodium silicate, microfine sand, iron oxides and manganese oxides), dispersing agents, set retarding agents, set accelerating agents, fluid loss control agents, strength retrogression control agents, and viscosifying agents well known to those skilled in the art.

[0016] The following examples are illustrative of the methods and compositions discussed above.

EXAMPLE 1

[0017] Components in the amounts listed in **TABLE 1** were added to form four batches of a normal density slurry. The batches were prepared according to API Specification RP 10B, 22nd Edition, 1997, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety).

[0018] The cement for all batches was Class A cement. The cement amounts are reported as percentages by weight of the composition ("%"). The water and zeolite amounts in this example are reported as percentages by weight of the cement ("%bwoc"). The density was conventionally measured, and reported in pounds per gallon ("lb/gal").

[0019] Zeolite was obtained from C2C Zeolite Corporation, Calgary, Canada, and mined from Bowie, Arizona, USA.

TABLE 1

Components	Batch 1	Batch 2	Batch 3	Batch 4
Water (%bwoc)	46.7	56.9	46.7	56.9
Cement (%)	100	100	100	100
Zeolite (%bwoc)	0	10	0	10
Density (lb/gal)	15.6	15.0	15.6	15.0
Temperature (°F)	40	40	60	60
Compressive strength @ 12 hours (psi)	190	322	555	726
Compressive strength @ 24 hours (psi)	300	753	1450	1507
Compressive strength @ 48 hours (psi)	- -	1554	2500	2600

TABLE 1 shows that batches with zeolite (Batches 2 and 4) had higher compressive strengths than conventional cement slurries (Batches 1 and 3).

EXAMPLE 2

[0020] Components in the amounts listed in **TABLE 2** were added to form four batches of a lightweight pozzolanic

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slurry. The batches were prepared according to API Specification RP 10B.

[0021] The cement for all batches was Class C cement. Zeolite was the same as in **EXAMPLE 1**. Fumed silica was obtained from either Fritz Industries, Mesquite, Texas, USA, or Elkem Group, Oslo, Norway.

TABLE 2

Components	Batch 1	Batch 2	Batch 3	Batch 4
Water (%)	110	110	110	110
Cement (%)	100	100	100	100
Fumed silica (%bwoc)	22	0	22	0
Zeolite (%bwoc)	0	22	0	22
Density (lb/gal)	12.0	12.0	12.0	12.0
Temperature (°F)	80	80	180	180
Compressive strength @ 12 hours (psi)	79	61	743	704
Compressive strength @ 24 hours (psi)	148	133	944	900
Compressive strength @ 48 hours (psi)	223	220	1000	921
Compressive strength @ 72 hours (psi)	295	295	1000	921
Thickening Time (hr:min)	5:20	4:03	5:43	4:15
Plastic Viscosity (cP)	41.4	49.9	16.9	18.3
Yield point (lb/100ft ²)	23.6	25.3	12.3	10.3

TABLE 2 shows that batches with zeolite (Batches 2 and 4) are an acceptable substitute for conventional fumed silica cement slurries (Batches 1 and 3).

EXAMPLE 3

[0022] Components in the amounts listed in **TABLE 3** were added to form five batches of a lightweight microsphere slurry. The batches were prepared according to API Specification RP 10B.

[0023] The cement for all batches was Class C cement. Zeolite and fumed silica were the same as in **EXAMPLE 2**. Each batch also contained 50% bwoc cenospheres (hollow ceramic microspheres), such as are available from Q Corp., Chattanooga, Tennessee, USA.

TABLE 3

Components	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Water (%bwoc)	98	98	98	98	98
Cement (%)	100	100	100	100	100
Fumed silica (%bwoc)	0	0	0	15	0
Zeolite (%bwoc)	0	15	0	0	15
Density (lb/gal)	11.5	11.5	11.5	11.5	11.5
Temperature (°F)	120	120	200	200	200
Compressive strength @ 24 hours (psi)	1107	1110	1202	2225	2026
Compressive strength @ 48 hours (psi)	1621	1734	1940	2669	2276
Compressive strength @ 72 hours (psi)	1942	1942	1789	2726	- -
Comments	settling	no settling	settling	no settling	no settling

TABLE 3 shows that batches with zeolite (Batches 2 and 5) did not settle, leading the Applicants to propose that zeolite acts as an anti-settling agent, as does conventional fumed silica (Batch 4).

EXAMPLE 4

[0024] Components in the amounts listed in **TABLE 4** were added to form three types of an 11.7 lb/gal density slurry. The types were prepared according to API Specification RP 10B. The cement for all batches was Class C cement.

5 Fumed silica was the same as in

EXAMPLE 2.

[0025] Slurry type 1 was a conventional slurry containing prehydrated bentonite. Bentonite was obtained from Haliburton Energy Services, Inc., Houston, Texas USA, and is sold under the trademark "AQUA GEL GOLD."

[0026] Slurry type 2 was a conventional slurry containing a 5% bwoc accelerating additive (1% sodium meta silicate; 2% sodium sulfate; 2% calcium chloride), 1% bwoc prehydrated bentonite, and 19% bwoc fly ash. Fly ash was obtained from Ascor Technologies, Calgary, Alberta, Canada (samples obtained at Sheerness and Battle River).

[0027] Slurry type 3 was a slurry according to one embodiment of the present invention. Zeolite is given as a percentage by weight of the composition. Zeolite was obtained from C2C Zeolite Corporation, Calgary, Canada, and mined from Princeton, BC, Canada. The zeolite was further divided by particle size, i.e., its ability to pass through conventional mesh screens (sizes 1,2, 3, etc.).

TABLE 4

Components	Type 1	Type 2	Type 3
Water %	154	114	130
Cement %	100	60	60
Bentonite %bwoc	4	1	0
Fly ash %bwoc	0	19	0
Fumed silica %bwoc	0	15	0
Zeolite (mesh size 1)%	0	0	30
Zeolite (mesh size 2) %	0	0	10
Density (lb/gal)	11.7	11.7	11.7
Time to 50 psi at 68°F (hr:min)	no set	4:43	9:21
Time to 50 psi at 86°F (hr:min)	no set	3:16	--
Time to 50 psi at 104°F (hr:min)	21:31	3:36	4:13
Time to 50 psi at 122°F (hr:min)	8:12	--	1:45
Time to 500 psi at 68°F (hr:min)	N/A	52:14	52:30
Time to 500 psi at 86°F (hr:min)	N/A	22:57	19:10
Time to 500 psi at 104°F (hr:min)	N/A	16:05	16:45
Time to 500 psi at 122°F (hr:min)	N/A	--	11:07

TABLE 4 shows that zeolite cement (Type 3) sets faster than conventional bentonite cement (Type 1) even at low temperatures, and delivers results similar to conventional fumed silica slurries (Type 2).

EXAMPLE 5

[0028] Components in the amounts listed in **TABLE 5** were added to form five batches of an 11.7 lb/gal density slurry. The batches were prepared according to API Specification RP 10B.

[0029] The cement for all batches was Class C cement. Zeolite was the same as in **EXAMPLE 4**. The accelerating additive for Batch 2 was calcium sulfate, the accelerating additive for Batch 3 was sodium aluminate, and the accelerating additive for Batches 4 and 5 was sodium sulfate.

TABLE 5

Components	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Water %	130	130	130	130	130
Cement %	60	60	60	60	60
Accelerating additive %bwoc	0	3	3	3	6
Zeolite (mesh size 1) %	30	30	30	30	30
Zeolite (mesh size 2) %	10	10	10	10	10
Density (lb/gal)	11.7	11.7	11.7	11.7	11.7
Temperature °F	122	122	122	122	122
Compressive strength @ 12 hours (psi)	1	347	258	196	356
Compressive strength @ 24 hours (psi)	104	355	531	360	745
Compressive strength @ 48 hours (psi)	400	748	903	687	847

TABLE 5 shows that zeolite cements set with all accelerating additives, as illustrated by the increasing compressive strengths.

EXAMPLE 6

[0030] Components in the amounts listed in TABLE 6 were added to form five batches of a 15.6 lb/gal slurry. The batches were prepared according to API Specification RP 10B. The cement for all batches was Class A cement. Zeolite and fumed silica were the same as in EXAMPLE 2. The dispersant was a sulfonated acetone formaldehyde condensate available from SKW Polymers GmbH, Trostberg, Germany.

[0031] Fluid loss was tested under standard conditions according to Section 10 of API Specification RP 10B, 22nd Edition, 1997, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety).

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TABLE 6

Components	Batc h1	Batc h2	Batc h3	Batc h4	Batc h5	Batc h6	Batc h7	Batc h8	Batc h9
Water %	46.6	47.8	49	46.0	47.8	49	45.8	47.8	49
Cement %	100	100	100	100	100	100	100	100	100
Zeolite %bwoc	0	5	10	0	5	10	0	5	10
Dispersant %bwoc	0	0	0	1	1	1	1.5	1.5	1.5
Density (lb/gal)	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6
Fluid loss at 80°F (cc/30min)	612	515	417	261	190	139	164	136	89
Fluid loss at 150°F (cc/30min)	590	482	417	328	110	91	287	--	69

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TABLE 6 shows that batches with zeolite (Batches 2, 3, 5, 6, 8, and 9) control fluid loss better than conventional cement. Also, the fluid loss control improves with increasing concentration of the dispersant.

EXAMPLE 7

[0032] Components in the amounts listed in **TABLE 7** were added to form five batches of a lightweight pozzolanic slurry. The batches were prepared according to API Specification RP 10B.

[0033] The cement for all batches was Class C cement. Zeolite and fumed silica were the same as in **EXAMPLE 2**. Under standard conditions set out in Section 15.6, Sedimentation Test, of API Specification RP 10B, 22nd Edition, 1997, of the American Petroleum Institute, the batches were placed in corresponding cylinders and allowed to set for 24 hours. Each cylinder was then divided into segments, and the density for each segment was determined by conventional means. It is understood that the absence of settling is indicated by minimal variation in density values among the sections of a given cylinder, as shown in **TABLE 7**.

TABLE 7

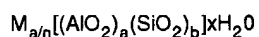
Components	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7
Water %	110	110	110	110	110	110	110
Cement %	56	56	56	56	56	56	56
Fumed silica %bwoc	22	0	22	0	0	22	0
Zeolite %bwoc	0	22	0	22	0	0	22
Initial density (lb/gal)	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Temperature (°F)	80	80	180	180	200	200	200
Settling Test Top Segment (lb/gal)	11.6	12.3	11.7	12.4	12.7	12.3	12.9
2nd Segment (lb/gal)	12.0	12.4	11.7	12.5	13.3	12.3	12.8
3rd Segment (lb/gal)	12.0	12.4	11.7	12.4	13.1	12.1	12.9
4th Segment (lb/gal)	11.9	12.4	11.8	12.3	--	--	--
5th Segment (lb/gal)	11.9	12.4	--	12.3	--	--	--
Comments	settling	no settling	no settling	no settling	settling	no settling	no settling

TABLE 7 shows that batches with zeolite (Batches 2, 4, and 7) did not settle.

[0034] In a preferred method of sealing a subterranean zone penetrated by a well bore, a cement composition comprising zeolite, cementitious material, and water is prepared. The cement composition is placed into the subterranean zone, and allowed to set therein.

Claims

1. A cement composition comprising: zeolite, cementitious material, and water.
2. A composition according to claim 1, wherein the zeolite is represented by the formula:



where M is a cation such as Na, K, Mg, Ca, or Fe; and the ratio of b:a is from greater than or equal to 1 to less than or equal to 5.

- 5 3. A composition according to claim 1 or 2, wherein the zeolite is analcime (hydrated sodium aluminum silicate); chabazite (hydrated calcium aluminum silicate); harmotome (hydrated barium potassium aluminum silicate); heu-landite (hydrated sodium calcium aluminum silicate); laumontite (hydrated calcium aluminum silicate); mesolite (hydrated sodium calcium aluminum silicate); natrolite (hydrated sodium aluminum silicate); phillipsite (hydrated potassium sodium calcium aluminum silicate); scolecite (hydrated calcium aluminum silicate); stellerite (hydrated calcium aluminum silicate); stilbite (hydrated sodium calcium aluminum silicate); or thomsonite (hydrated sodium calcium aluminum silicate).
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4. A composition according to claim 1, 2 or 3, wherein the zeolite is present in an amount of from 1% to 95%, preferably from 5% to about 75%, by weight of the cementitious material in the composition.
- 15 5. A composition according to claim 4, wherein the zeolite is present in an amount of from 30% to 90%, preferably from 50% to 75%, by weight of the cementitious material in the composition.
6. A composition according to any of claims 1 to 5, wherein the cementitious material is Portland cement, pozzolan cement, gypsum cement, aluminous cement, silica cement, or alkaline cement.
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7. A composition according to any of claims 1 to 6, wherein the water is present in an amount of from 22% to 200%, preferably from 40% to 100%, by weight of the cementitious material.
8. A composition according to any of claims 1 to 7, further comprising an accelerating additive, preferably present in
25 an amount of from 0.5% to 10%, more preferably from 3% to 7% by weight, of the cementitious material.
9. A composition according to claim 8, wherein the accelerating additive is sodium chloride, sodium sulfate, sodium aluminate, sodium carbonate, calcium sulfate, aluminum sulfate, potassium sulfate, or alum.
- 30 10. A composition according to any of claims 1 to 9, further comprising a dispersant, eg a sulfonated acetone formal-dehyde condensate, said dispersant preferably being present in an amount of from 0.01 % to 2% by weight of the cementitious material.
11. A composition according to any of claims 1 to 10, further comprising cenospheres, preferably present in an amount
35 of from 30% to 60% by weight of the cementitious material.
12. A method of sealing a subterranean zone penetrated by a well bore, which method comprises cementing the zone with a cement composition as claimed in any of claims 1 to 11.

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EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 9 March 2004	Examiner Zimpfer, E
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EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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